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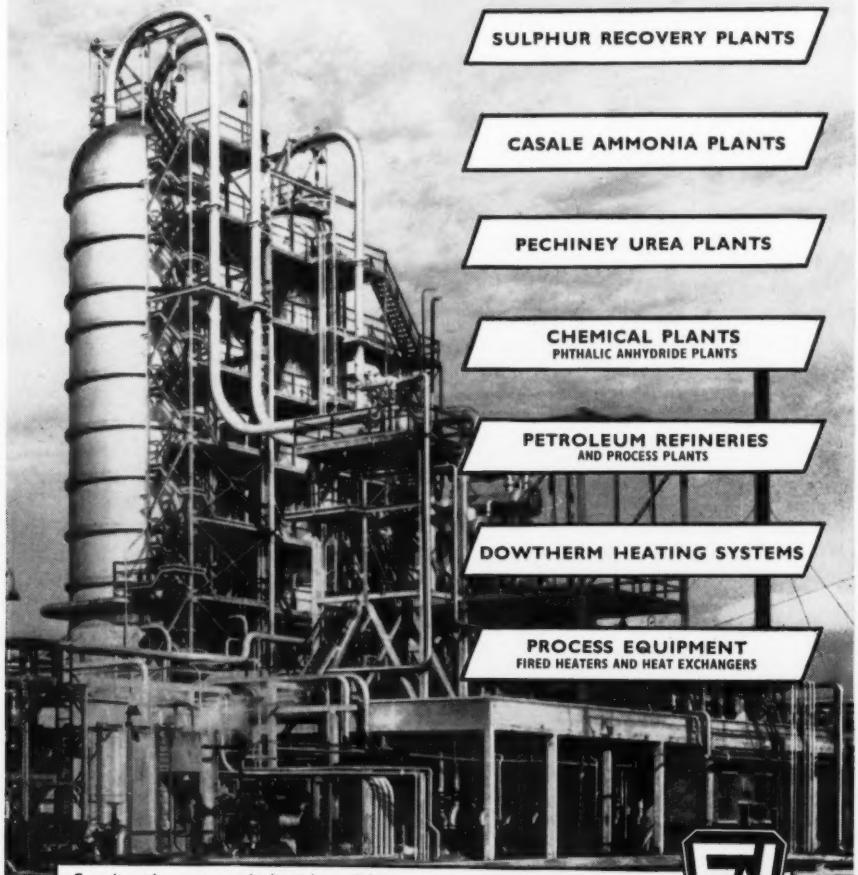

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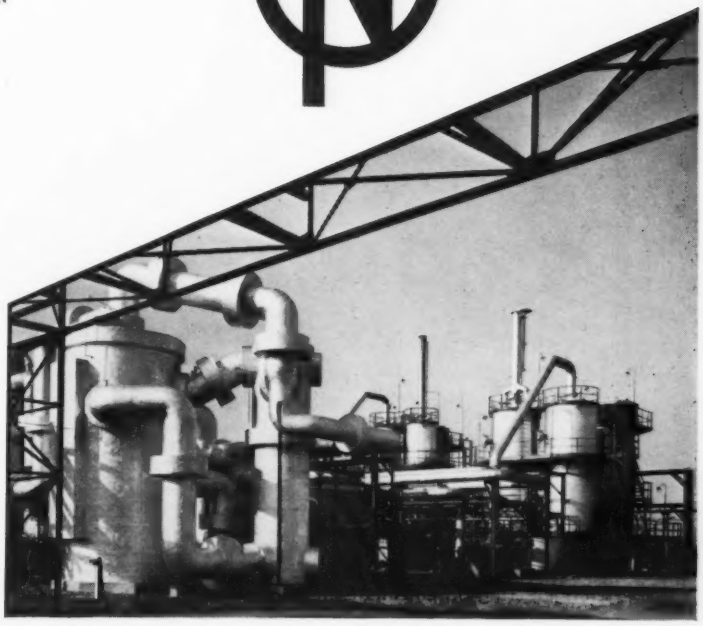

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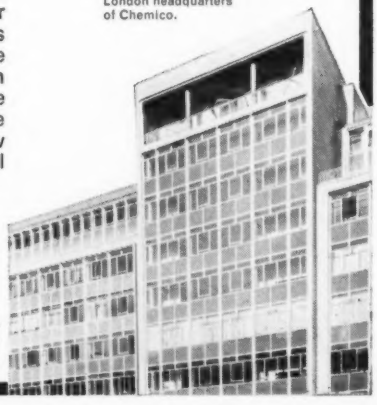

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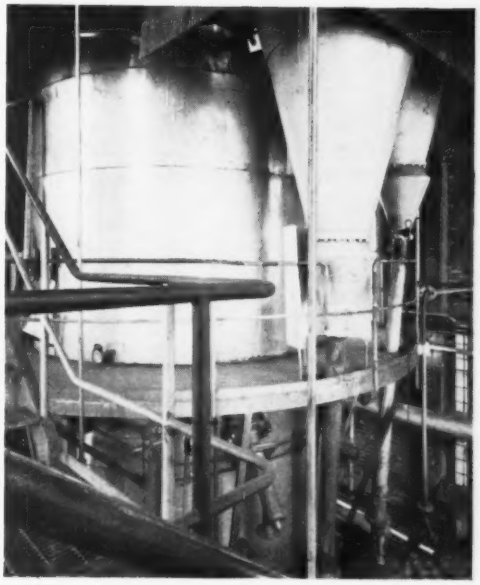
Novel Method of Fluidised Bed Roasting of Arsenical Pyrites

A LARGE PROPORTION OF THE PYRITES on the world market has an arsenic content that may make the residues unsuitable for iron extraction. When roasting pyrites in multiple-hearth furnaces the arsenic can be removed without any special measures. When using modern fluidised bed reactors of the Dorr or B.A.S.F. types too high a proportion of the arsenic remains in the residues in the form of iron arsenate, both on account of the time during which the flue dust is in contact with the roaster gases containing vapourised arsenic compounds and on account of the furnace temperature. The problem is of considerable importance and research has long been carried out in the U.S.A., West Germany and other countries. Some of the pyrites concentrates produced by the Bolidens Gruvaktiebolag of Stockholm suffer from a high arsenic content : the company has made experiments in collaboration with the Stroms Bruk Company using Dorr roasters ; and their process is now being used on an economic scale at Stroms Bruk and at two other plants also. Tests are being made with B.A.S.F. furnaces.



General view of the pyrites roaster showing the two cyclones.

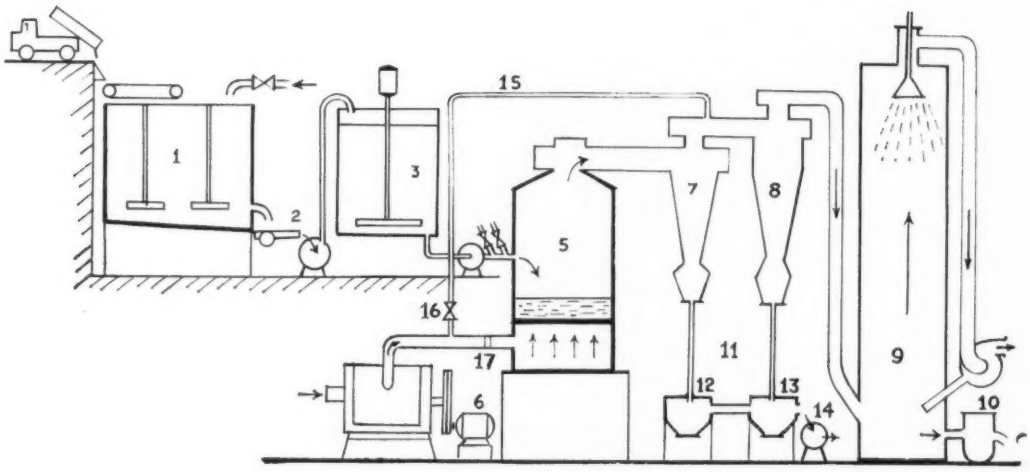
Iron arsenate is formed by the reaction:—

$$Fe_2O_3 + As_2O_3 + O_2 = 2FeAsO_4$$

It has been shown that this can be avoided with a restricted air intake. If the partial pressure of the oxygen falls below a certain value, in the first place oxidation of the arsenic does not occur ; without the formation of arsenic oxides iron arsenate cannot result. In the second place the iron is not oxidised to hematite (Fe_2O_3), but only to magnetite (Fe_3O_4), with which arsenic oxides less readily combine. However if the partial oxygen pressure falls too low, part of the iron sulphide remains unaltered, and the residues have too high a sulphur content. When the partial pressure lies between these two values magnetite is formed but the exit gases have a certain elemental sulphur content which approaches zero at the lower value and which rises with falling partial oxygen pressure.

From the results of an investigation made by Schmahl*, the composition of the exit gases can be calculated at the approximate furnace temperature of 900°C and at varying partial oxygen pressures. From this it appears that it is theoretically possible to roast pyrites to magnetite with very little sulphur sublimation. In practice however it is probably impossible to regulate the air-pyrites relationship with sufficient precision, and considerable sublimation must be expected. Elemental sulphur in the exit gases would condense in the washing tower and choke the tower and pipes as well as being a waste. A method has therefore been evolved by which the elemental sulphur is burned by secondary air introduced after the cyclones have separated the hot pyrites residues from the gases.

* Archiv fur Huttenwesen. 1954, page 315.



1. Slurry Mixing Tank. 2. Centrifugal Pump. 3. Storage Tank. 4. Diaphragm Pump. 5. Dorr Roaster. 6. Air Compressor. 7. First Cyclone. 8. Second Cyclone. 9. Washing Tower. 10. Waste. 11. Pipes for Pyrites Residues. 12 & 13. Containers for Cooling Water and Gas Trap. 14. Centrifugal Pump for Pyrites Residues Slurry.

Fig. 1—Flow diagram of the Pyrites Roasting Plant at the Ströms Bruk Works.

The flow sheet of the Stroms Bruk plant is shown in Figure 1. An agitator mixes the concentrates with water and the slurry obtained is pumped via storage tanks to the roaster. Cooling of the furnace is effected by the moisture in the concentrates while accurate temperature control is achieved by injecting additional quantities of water into the combustion chamber. The exit gases from the roaster pass through two cyclones, and the remaining residue dust is removed by water sprayed into the washing tower, at which stage the vapourised arsenic compounds from the pyrites condense and are thus separated from the gases. The slime runs to waste. Since only about 2% of the pyrites residues are separated in the second cyclone, further air can be introduced into the gases at this stage, despite the possibility of the formation of hematite and hence iron arsenate. The secondary air is introduced into the flue gas inlet through a 75 mm. pipe from the main air stream and represents about 8% of the total quantity of air. After the introduction of the secondary air the sulphur dioxide content of the gas is about 15%. There is no problem of sublimed sulphur.

The plant has been in continuous operation since October 1958. The following results have been obtained :—

% Arsenic content of pyrites concentrates	% Arsenic content of residues 1st Cyclone	2nd Cyclone	% Sulphur content of residues
0.12—0.16	0.01—0.03		0.44
0.24	0.04	0.05	0.5
0.39	0.06	0.07	0.5

Thus the system has proved satisfactory when roasting pyrites concentrates having an arsenic content of 0.12–0.39%. To meet the requirements of the German steelworks, which buy most of the residues from the Swedish pulp mills, their arsenic content must not exceed 0.06-0.07%. This can be achieved when the arsenic content of the pyrites does not exceed 0.4%. The residues obtained consist chiefly of magnetite with a sulphur content of about 0.5%. Magnetite residues have a higher iron content than hematite and are also easier to sinter.

We are indebted to Messrs. J. Morath and K. G. Görling of Bolidens Gruvaktiebolag for the information and illustrations kindly placed at our disposal.

Developments in Desulphurisation

The source of world sulphur supply in which the most important developments are now occurring is undoubtedly that of sulphur recovered from sour gas streams. Hence a great amount of research has been undertaken for the improvement of existing desulphurisation processes and for the invention of new ones. What appear likely to be some of the most important of recent developments in this field are the theme of the following articles.

In Europe the hot carbonate process has long been an established method of treating coal gas, but its application in the United States to hydrocarbon gas streams is a comparatively recent thing. Since it is claimed that the Giammarco-Vetrocoke process is a considerable improvement on conventional hot carbonate removal, it seems likely that the relative position of the hot carbonate process as compared with the amine process will be made stronger than appears from the careful cost comparison made some time ago by Mr. A. G. Eickmeyer. A more radical innovation is that of the Atlantic Refining Company, whose laboratory experiments indicate that sulphur can be recovered directly from sour gases, without an absorption system, by using ferric chloride as an oxidising agent. Yet another approach is that of two research workers at Kansas University who have evolved at a theoretical stage a process for hydrogen sulphide removal by freezing the sour gas stream.

On the face of it there appear to have been fewer developments in the desulphurisation of coal gas, although Messrs. Harpener Bergbau G.m.b.H. have modified the normal hydrogen sulphide removal by ammonia washing to adapt it to gases having a high proportion of hydrogen sulphide.

HOT CARBONATE PROCESS COSTS WITH HYDROCARBON FEEDSTOCK

THE HOT CARBONATE PROCESS is now employed in at least seven plants in the United States alone. So far its major applications have been in the petrochemical field. Hot carbonate units may be used for treating natural gas and are also applicable to synthetic ammonia plants where the removal of carbon dioxide, which is damaging to the catalyst, must be so thorough as to leave only a few parts per million. The process is also being used in the production of hydrogen and for cleaning recycle ethylene in an ethylene oxide plant.

The essence of the process is the absorption under pressure of acid gas components such as carbon dioxide and hydrogen sulphide by a hot solution of potassium bicarbonate. Bicarbonate ions are always present in this circulating solution. During the removal of carbon dioxide the reactions involve an increase or a decrease in the proportion of bicarbonate as the solution cycles between the absorption and stripping towers. Absorption takes place at substantially the same temperature as is subsequently used for low pressure steam regeneration. Similar reactions occur during the absorption of hydrogen sulphide, which in solution becomes the hydro-sulphide ion. Ordinarily a sequence is employed consisting of two or three stages of carbon dioxide removal, the bulk of the gas being absorbed by the bicarbonate solution at the first stage. The carbon dioxide content of the effluent gases from hot carbonate units varies from 3% to less than 0.2%, though plants can be designed to remove even more carbon dioxide than this.

Although the hot carbonate process has not yet been used commercially for the removal of large quantities of hydrogen sulphide, a plant for treating sour natural gas is now being built and is expected to be in operation by the end of 1959. Pilot plant experiments on a gas containing both carbon dioxide and

hydrogen sulphide have been carried out by the U.S. Bureau of Mines. Data from these tests is shown below :—

TABLE I Mixed $H_2S - CO_2$ Removal

Feed Stream*		Effluent	
Composition, %		*Composition*, %	
CO_2	H_2S	CO_2	H_2S
11.3	0.51	0.33	0.002
11.0	0.556	0.40	0.004
10.9	0.578	0.34	0.004
10.7	0.927	0.23	0.011
11.5	4.4	0.1	0.01

*Feed gas at 300 psig.

It will be seen that the ratio of inlet concentration to outlet concentration is very much higher for hydrogen sulphide than for carbon dioxide. The hot carbonate removes hydrogen sulphide preferentially. This is thought to be because hydrogen sulphide is itself an acid while carbon dioxide must first dissolve in water before becoming such.

Gas Pressures

The hot carbonate method is not recommended for low pressure absorption, or for high pressure absorption of a low concentration of acid gas. As a general principle, when the partial pressure of acid gas is 20 psi or more, a hot carbonate unit should be considered, although this rule may require modification depending on plant size and local costs.

Under favourable conditions of pressure and acid gas content, both the initial investment and operating costs are considerably less than for amine plants, principally because the use of a hot carbonate solution obviates the necessity for expensive heat exchangers, and less steam generation and cooling equipment is needed. In addition, because hot carbonate units require less heat than that needed for amine regeneration, waste heat recovery is frequently practical. It is possible to use low pressure steam generated either by cooling gas-engine drives with water, or by the recovery of surplus heat from process streams.

A comparative study of the hot carbonate and mono-ethanolamine processes is set out in Table II and in Figures 2, 3 and 4. It is based on meeting a pipe-line specification of 0.25

TABLE II

Comparative Costs for Hot Carbonate and Monoethanolamine Processes

	5% acid gas content		*10% acid gas content*		*20% acid gas content*	
	Hot carbonate	MEA	Hot carbonate	MEA	Hot carbonate	MEA
Investment including utilities (000 dollars)	1,600	1,450	1,890	2,360	2,465	4,150
Operating cost p.a. (000 dollars) ..						
Labour and supervision	100	100	100	100	100	100
Maintenance (4% of capital)	64	58	75	94	98	166
Fuel Gas (20 c/million Btu)	112	206	150	412	230	824
Chemicals	10	20	12	25	16	35
Fixed charges (16% of capital)	256	232	303	378	395	664
Total	542	616	640	1,009	839	1,789
Cost per thousand cu. ft. of gas treated (cents)	1.55	1.76	1.83	2.88	2.40	5.11
Cost per thousand cu. ft. of gas removed (cents)	31.0	35.2	18.3	28.8	12.0	25.6

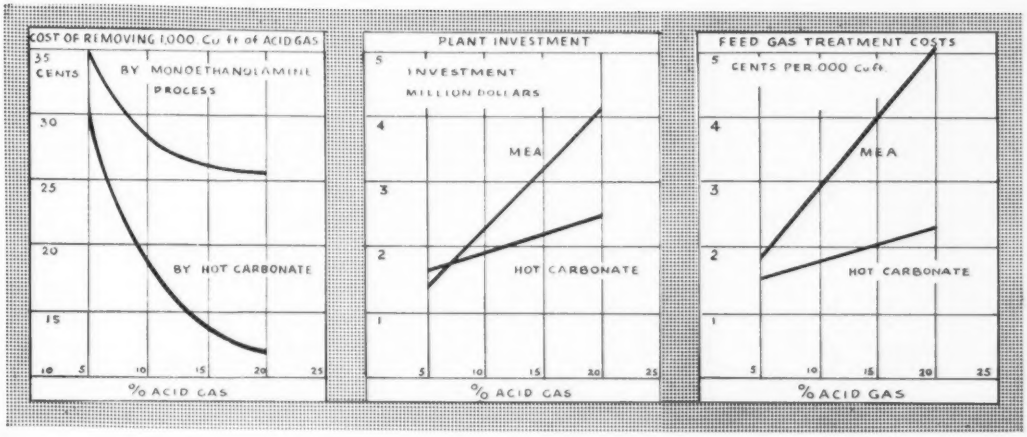


Fig. 2 *Fig. 3* *Fig. 4*

grains of sulphur per 100 cu. ft. Differing acid gas concentrations have been tried. The results are from treatment plants having a feed capacity of 100 million cu. ft. of gas per day and an absorption pressure of 500 psig. Amine plants assume 15% MEA, and a net concentration of 0.3 mole of acid gas per mole of amine is generally recommended to avoid corrosion. This corresponds to 2.32 cu. ft. of acid gas per gallon of solution and a solution circulation rate directly proportional to the solution's acid gas content. Hot carbonate design assumes a 30% potassium carbonate solution and an acid gas content varying from 2.1 to 4.2 cu. ft./gallon depending on the partial pressure.

It will be seen from Figures 3 and 4 that costs with an amine plant increase sharply with acid gas concentration. This is because of the limit set to the acid gas content of the amine to avoid corrosion, in turn resulting in a high circulation rate and steam consumption. The hot carbonate process, on the other hand, makes more effective use of the available pressure of acid gas, and in consequence the costs increase more slowly with acid gas concentration. It appears that the two lines in Figure 4 would intersect at an acid gas concentration of 4%, indicating that at this point costs would be about the same for either method. Here, the total pressure of 500 psig corresponds to a partial pressure of 20 psi, and from this the general rule may be deduced. The investment cost data is for an entire plant, including steam generation and cooling systems, but excluding plant site and housing for personnel.

Corrosion

When carbon dioxide is the only acid gas component to be removed, about 3,000 parts per million of potassium dichromate has proved to be a corrosion inhibitor. However, this will react with hydrogen sulphide, and a satisfactory inhibitor for sour gas purification is still needed. An alternative is the use of resistant construction materials. Carbon steel is generally satisfactory except for items in critical positions. A stainless steel such as Type 316 is ordinarily used for the letdown valve and for the rotating elements of the pumps. A knowledge of the suitability of the materials for pump casings has so far been confused by the occurrence of cavitation. In the instance of one hot carbonate plant, pumps suffered severely both from corrosion and erosion, though later with more favourable conditions the carbon steel casings proved satisfactory. Table III summarises pump corrosion experience at a variety of plants.

TABLE III **Pump Corrosion Experience at Seven Hot Carbonate Plants**

Original pumps	Materials	Performance	Replacements
Two-stage centrifugal. 857ft. head at 564 gpm.	Cast iron case, cast iron impeller.	Severe corrosion-erosion of impeller and casing after 100 hr. operation. Trace of H_2S in feed gas.	Same pump with 316 SS case and impeller, 316 SS Stellite wear rings.
Vertically split single-stage, double-suction, 3,550 r.p.m.	Cast steel case, cast iron impeller.	Erosion-corrosion of impeller after 3 weeks. Packing with water purge. Some noise, possibly cavitation.	Spare pump, same as original, with 304 SS case and impeller. Not in service.
Two-stage 3,600 r.p.m. 800ft. head at 115 gpm.	Cast steel case, cast iron impeller, cast iron wear rings.	Trace of H_2S in gas. Erosion-corrosion of cast iron impeller and case after 4 weeks.	Same pump with 316 SS case impeller and wear rings.
Three-stage, 1,750 r.p.m.	Cast iron case, bronze impeller.	Original : poor suction head ; cavitation. Corrosion of wear rings. Impeller lasted 30 days, replacement impeller lasted 60 days, wear at interstage seals. Present pumps maintain 3,000 ppm inhibitor. No corrosion in 1 year.	1st replacement had carbon steel case and impeller. Present pump same with 6-stage booster ; 3—4% Ni cast iron case, 316 SS impeller.
Two-stage, 3,500 r.p.m.	Cast iron case, 304 SS impeller, 304 SS wear rings.	Inadequate suction head, cavitation. Impeller lasted 3 months.	New pump, all stainless steel.
Two-stage, 3,550 r.p.m.	11 — 13% chrome case, impeller and wear rings.	Rapid corrosion occurred when gas contained H_2S, which poisoned dichromate inhibitor.	Same pump with 316 SS case, impeller and sleeves. Stellite wear ring facing.
Single-stage, 3,850 r.p.m.	Cast steel case, Cu-free Ni-resisting impeller, 11—13% chrome wear rings.	Cavitation, general corrosion. Erosion-corrosion of case and impeller.	Single-stage, 1,750 r.p.m. booster pump added. 4—6% chrome case.

Another consideration is that since potassium carbonate solution is an electrolyte, both the absorber and regenerator vessels must be stress-relieved to avoid corrosion from stress.

Conclusion

The hot carbonate process shows considerable advantages over the amine process for removing acid gases with a high partial pressure. For carbon dioxide removal it has already been proved satisfactory and it may be recommended for improving the calorific value of sweet natural gas, although with sour gas corrosion problems are as yet imperfectly understood. The limitations to the applicability of any cost comparison are nevertheless evident on two accounts. First, with hot carbonate plants there are a number of variable factors. Among these are the compositions of the solution and gas, absorption and regeneration pressures, absorption temperature, steam requirements, circulation rate, vessel configuration, and either the number and type of trays or the packing material and height of packed beds. The ability of both the designer and the operator is clearly of great importance. Second, costs and methods of cost accounting vary so much from one country to another that no comparison will hold generally. This table relates specifically to the United States.

THE GIAMMARCO-VETROCOKE PROCESS

IN THE GIAMMARCO-VETROCOKE PROCESS, which is suitable for removing acid gases from natural or synthetic gas, the absorbant solutions are of sodium and potassium carbonate containing tri- and pentavalent arsenic. Their selectivity for hydrogen sulphide in the presence of carbon dioxide is controlled by additives which reduce the rate at which carbon dioxide is absorbed. Such additives are arsenic oxide and selenious and tellurous acids. Hydrogen sulphide and carbon dioxide can be removed separately or in the same plant.

It is claimed that the new process has a number of advantages over the monoethanolamine (MEA) process and also over the conventional hot carbonate process. Losses of amine occur in the monoethanolamine process. Corrosion is a considerable problem with the conventional hot carbonate process, whereas with the Giammarco-Vetrocoke process the treating solution is non-corrosive.

Regenerating the solution with the new process requires a smaller steam consumption than with either of the two older processes, and air may be used instead of steam. According to the Fluor Corporation Limited, the licensed plant constructors in the U.S.A., the costs per thousand standard cubic feet of gas treated by the various processes are as follows :—

Process	*Cost per 1,000 s. c. f.*
Giammarco-Vetrocoke	
Steam Generation	4.1
Air Generation	4.8
Potassium Carbonate	8.2
Aqueous MEA	10.1

This assumes a natural gas stream of 90 million cu. ft. per day at a pressure of 1,000 p.s.i.g. and a temperature of 100°F, containing 28% by volume of carbon dioxide and two grains per 100 s.c.f. of hydrogen sulphide.

The Giammarco-Vetrocoke process is already in use at several plants in Europe and at least one plant based on it is now being built for the removal of hydrogen sulphide and carbon dioxide from natural gas in the U.S.A. The Power-Gas Corporation Ltd. is licensed to build such plants in the United Kingdom.

NEW DESULPHURISATION PROCESS

BY THE ATLANTIC REFINING COMPANY

THE MOST WIDELY USED COMMERCIAL METHOD of converting hydrogen sulphide to elemental sulphur is by combustion in Claus kilns, the reaction being simply :—

$$2H_2S + O_2 = 2H_2O + 2S$$

But a combustion process can clearly be used only in connection with a system in which hydrogen sulphide is separated from the other constituents of a sour gas stream. It was also thought that an oxidation process not employing combustion might show advantages over the Claus process in both control and efficiency.

For such a process a reagent would be required having a multi valent ion which will oxidise hydrogen sulphide and in turn itself be oxidised by air. The Atlantic Refining Company has achieved success on a laboratory scale using an aqueous solution of ferric chloride with the addition of a chelating agent, " Versene Fe-3 Specific ", giving a " ferric versenate " solution. The ferric chloride oxidises the hydrogen sulphide to elemental sulphur and becomes ferrous chloride, which is then oxidised to the ferric form by oxygen:—

$$H_2S + 2FeCl_3 = 2FeCl_2 + 2HCl + S$$

$$4FeCl_2 + 4HCl + O_2 = 4FeCl_3 + 2H_2O$$

From these equations it will be seen that the net result is that achieved by the Claus process—the oxidation of hydrogen sulphide to elemental sulphur with the production of water.

What promises to be a great advantage of the new process is that it is thought that it will obviate the need for a separate system for removing hydrogen sulphide from other gases. To convert hydrogen sulphide to elemental sulphur, hydrogen sulphide and air would probably just be passed through an iron versenate solution. To remove hydrogen

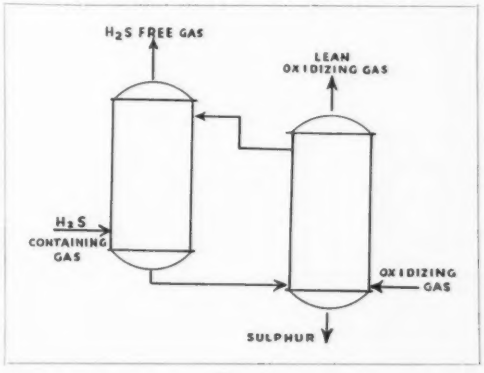


Fig. 5

sulphide from a hydrocarbon gas stream at the same time as producing elemental sulphur from it, a modification would be needed to avoid contaminating the hydrocarbon gas with unconsumed air. For this the oxidation of the hydrogen sulphide would take place in a separate chamber from that for the oxidation of ferrous to ferric chloride, as illustrated in Figure 5. In both operations the pH of the

iron versenate solution would be above 5 and its concentration adjusted to the proper level to obtain complete conversion of the hydrogen sulphide at a temperature high enough to remove the water formed in the reaction.

The removal of sulphur from the reaction mixture has not as yet been thoroughly investigated. The sulphur is formed as a finely divided solid which settles rapidly. It can be separated by decantation or filtering, but the sulphur thus produced would require washing with water or dilute acid to give a product free of iron. It thus seems better to separate the sulphur as a liquid. As it has been found that the iron versenate reagent is stable above the melting point of the sulphur, there is no reason why this cannot be done.

Although the process has been studied so far only in the laboratory, no problems have been revealed which would indicate difficulties in increasing the scale of operations. A Patent Application has been filed.

EXPERIMENTS AND RESULTS

A survey of the standard electrode potentials showed several multivalent ions which could oxidise hydrogen sulphide and in turn be oxidised by oxygen. Of these, iron seemed to be the most advantageous to study. The sulphur produced in the experiments was measured by filtering the used solution, drying the sulphur, and weighing it. Unconverted hydrogen sulphide was determined by iodometric titration of the effluent gas. The total iron and the ferric-ferrous ion concentrations were determined by titration with ceric sulphate using ferroin as an indicator. A few experiments showed that an aqueous ferric chloride solution will oxidise hydrogen sulphide to elemental sulphur rapidly and stoichiometrically according to the first equation given above.

However when the hydrogen sulphide and air were together passed into a ferric chloride solution the amount of sulphur produced was only that expected from the reduction of the ferric chloride initially present—0.5 molecules of sulphur per molecule of chloride (Run 1, Table I). A few experiments on the oxidation of ferrous chloride with air and with pure oxygen showed that the rate of oxidation of ferrous to ferric chloride was too slow to keep pace with the rapid oxidation of the ferric chloride (Runs 2-7, Table 1). Some method of increasing the oxidation rate of the ferric ion was needed for this reagent to be used in a continuous process. Agitation was found to help the reaction to some extent (Runs 6 and 7, Table I). However a satisfactory solution to the problem by some mechanical means of increasing the availability of oxygen appeared impracticable.

TABLE I — **Oxidation of H_2S by Aqueous $FeCl_3$**

Run No :	1	2	3	4	5	6	7
Solution	$FeCl_3$	$FeCl_2$	$FeCl_2$	$FeCl_2$	$FeCl_2$	$FeCl_2$	$FeCl_2$
Moles Fe	0.0940	0.0918	0.0918	0.0918	0.0895	0.134	0.139
Molarity of solution	0.940	0.918	0.918	0.918	0.895	0.895	0.930
Temperature (°C)	26.0	27.0	61.2	90.0	67.0	60.0	60.0
Time (hours)	1.0	1.0	1.0	1.0	1.0	1.0	2.7
H_2S (moles per hour)	0.094	0	0	0	0	0	0.048
O_2 (moles per hour)	(air) 0.094	(air) 0.094	(air) 0.094	(air) 0.094	0.79	0.79	0.79
Stirring	No	No	No	No	No	Yes	Yes
Moles sulphur ÷ moles Fe	0.497	—	—	—	—	—	0.316
*Mole per cent. sulphur received ..	0	—	—	—	—	—	33.9
Mole per cent. Fe^{+++} of total Fe	3.2	0	2.1	3.3	8.2	26.8	25.8

*Sulphur from stoichiometric reduction of Fe^{+++} originally present not included.

Use of Chelating Agent

Ferric chloride solutions are acidic and the rate of oxidation of ferrous to ferric ion should be increased if the pH of these solutions could be raised. Since one cannot exceed a pH value of 7 without precipitating highly insoluble ferric hydroxide, some mechanism such as chelation would be necessary to hold the iron in solution at higher pH values. The question then arose whether such chelated iron solution would be suitable for an oxidation-reduction system; and the results given in Table II show that they are.

Chelated iron solutions of ferric versenate were made by dissolving ferric chloride in water and slowly adding to it as a ligand the "Versene Fe-3 Specific". The active compound in the agent is the sodium salt of N,N di (∝ hydroxy ethyl) glycine. This solution has a pH value of 12 when measured in a 1% concentration. Since the Versene was basic and the ferric chloride solution acidic, considerable heat was evolved. The resulting dark red solution was acidic and adjustment of its pH value was achieved by the addition of ammonium hydroxide, or 20% sodium hydroxide, while stirring vigorously to avoid local over-concentrations of the base and consequent precipitation of the iron as ferric hydroxide. The 1:1 molecular ratio of Versene to ferric ion is suitable for pH values up to 8, but for pH values higher than this the molecular ratio must be 2:1 or higher.

The solution as used had a pH value of 1.2. It was shown that this solution will oxidise hydrogen sulphide to sulphur and also that the oxygen passed in with the hydrogen sulphide appeared to bring about some oxidation of the ferrous to ferric chloride, since the molecules of sulphur produced per molecule of oxidant (Fe^{+++}) was greater than 0.5 (Run 1, Table II). However the percentage of moles of sulphur recovered from the hydrogen sulphide was only 31%, including the sulphur precipitated by the ferric chloride originally present. Since there was very little ferric ion left in the solution at the end of the run, it was clear that the re-oxidation of the ion was too slow for a practical system.

When the pH value of the ferric versenate solution was raised to 5.5 or more the system worked very much better (Runs 2-4, Table II). Essentially all of the hydrogen sulphide was converted to sulphur and the ferric ion content of the solution at the end of the run was more than 90%. These runs indicate that at these pH values the oxidation of the ferrous

TABLE II **Oxidation of H_2S by Ferric Versenate**

Run No. :	1	2	3	4	5	6
Solution	Ferric Versenate	Ferric Versenate	Ferric Versenate	Ferric Versenate	Versene only	NaOH only
Moles Fe	0.117	0.0949	0.0941	0.0931	0.10	0.075
Molarity	0.779	0.633	0.628	0.621	0.666	0.50
pH	1.2	5.5	8.5	8.4	12.6	12.7
Temperature (°C.)	24.0	26.0	30.0	29.0	27.0	27.0
Time (hours)	2.0	4.7	3.0	4.0	4.0	18.7
H_2S (moles per hour)	0.048	0.048	0.048	0.048 (air)	0.048	0.048
O_2 (moles per hour)	0.79	0.79	0.79	0.65	0.79	0.79
Moles sulphur ÷ moles oxidant	0.641	2.38	1.49	2.02	0.531	0.455
*Mole per cent. sulphur received	30.8	100.0	97.0	97.2	27.7	3.8
Mole per cent. Fe^{+++} of total Fe	0.7	93.4	97.0	97.5	—	—

*Sulphur from stoichiometric reduction of Fe^{+++} originally present not included.

to the ferric ion was as rapid as the oxidation of the hydrogen sulphide to sulphur, and that the solution could consequently be used in a continuous process. The Versene and the sodium hydroxide by themselves give only partial conversion of the hydrogen sulphide, but do form some sulphur when hydrogen sulphide and oxygen are passed in concurrently (Runs 5 and 6, Table II).

Removal of Water

The oxidation of hydrogen sulphide results in the production of one molecule of water per molecule of hydrogen sulphide. The easiest way to remove this water would be to operate the system at a temperature at which the water would be driven off as vapour. The temperature required for maintaining a desired concentration of the reagent would be a function of the partial pressure of the hydrogen sulphide in the gas to be treated. The higher the molecular fraction of the hydrogen sulphide the higher would be the temperature required to remove the water formed in the oxidation.

It was shown that at a temperature of 100°C a marked drop occurs in the efficiency of conversion to sulphur when hydrogen sulphide and oxygen are concurrently passed into a ferric versenate solution of a pH value of 7 (Run 1, Table III). Since all the iron in the solution was in the ferric state it appears that the higher temperature adversely affected the oxidation of the hydrogen sulphide but not the regeneration of the ferric ion. This was probably due to the lower absorption of hydrogen sulphide at the higher temperature. Hydrogen sulphide passed into the same solution at the same temperature but without the addition of oxygen resulted in the stoichiometric formation of sulphur (Run 2, Table III). Eliminating the oxygen flow through the reagent apparently helped the reaction by improving the absorption of hydrogen sulphide. The used solution was easily re-oxidised to the ferric state (Run 3, Table III).

TABLE III

Oxidation of H_2S by Ferric Versenate at 100°C. and pH = 7.0

Run No. :	1	2	3
Moles Fe	0.0964	0.0994	0.994
Molarity	0.643	0.664	0.664
Time (hours)	7.0	1	1
H_2S (moles per hour)	0.048	0.048	0
O_2 (moles per hour)	0.79	0	0.79†
Moles sulphur ÷ moles Fe	1.591	0.483	—
*Mole per cent sulphur received	38.2	—	—
Mole per cent. Fe^{+++} of total Fe	100	0	100

† 0.65 mole per hour O_2 as air gives same results.

*Sulphur from stoichiometric reduction of Fe^{+++} originally present not included.

Sour Hydrocarbon Gas Stream

The sample of hydrocarbon gas used was a "stabilizer gas" from a catalytic cracking unit and its analysis was as follows :—

CH_4	1%
C_3H_6	30%
C_4H_8	2%
C_2H_6	10%
C_3H_8	52%
C_4H_{10}	2%
H_2S	5%

This gas was passed through the iron versenate reagent under the conditions indicated and alternately with the regenerated air to avoid dilution of the sweetened gas. The hydrogen sulphide was completely converted to sulphur at 27°C (Run 1, Table IV). When the temperature was raised to 100°C, only 69% was converted (Run 2, Table IV). However virtually complete conversion was achieved at this temperature by increasing the concentration and pH value of the reagent (Run 3, Table IV).

TABLE IV

Oxidation of H_2S in Hydrocarbon Gas Stream by Ferric Versenate

Run No. :	1	2	3
Moles Fe	0.098	0.0994	0.138
Molarity	0.655	0.664	0.916
Time (hours)	1.0	1.0	1.0
pH	7.0	7.0	7.9
H_2S (moles per hour)	0.048	0.048	0.048
Temperature	27	100	100
*Mole per cent. sulphur received	100	68.6	99.8

*Mole per cent of total sulphur as H_2S.

HYDROGEN SULPHIDE REMOVAL FROM NATURAL GAS BY FREEZING

AN INTERESTING APPROACH to the removal of hydrogen sulphide from natural gas has recently been thought out by Messrs. U.K. Im and F. Kurata, both of Kansas University. Their process is one of refrigeration. On cooling a mixture of methane and hydrogen sulphide to the point of condensation, two liquids form and may be separated by decanting, assuming the feed gases have a molecular hydrogen sulphide content of about 7% or more. For further purification of the methane, the methane-rich liquid is cooled to a temperature at which hydrogen sulphide solidifies. Cooling to this lower temperature is necessary with feed gases having a molecular hydrogen sulphide content below about 7%, even if only low methane purity is required, as at such hydrogen sulphide concentrations two distinct liquids are not formed and hence liquid separation is impossible.

A flow diagram of the process with a liquid separator for feed gases having a hydrogen sulphide content of more than 7% is given in Figure 7. The compressed feed gas is initially divided into two streams for cooling. One of these the impure hydrogen sulphide from the liquid separator suffices to cool, expansion being used to lower the temperature of the cooling stream after the second heat exchanger and before the first. The other passes through two refrigeration units and two heat exchangers cooled by sweetened methane from the solid separator. The feed gas streams meet and pass into the liquid separator, where the bulk of the hydrogen sulphide is removed in the form of hydrogen sulphide-rich liquid. The methane-rich liquid passes through an expansion valve and the sudden chilling which results brings about the precipitation of the remaining hydrogen sulphide in solid form. In this vessel solid, liquid, and a composite state between liquid and gas are all at once present. It would of course be possible to extend the process

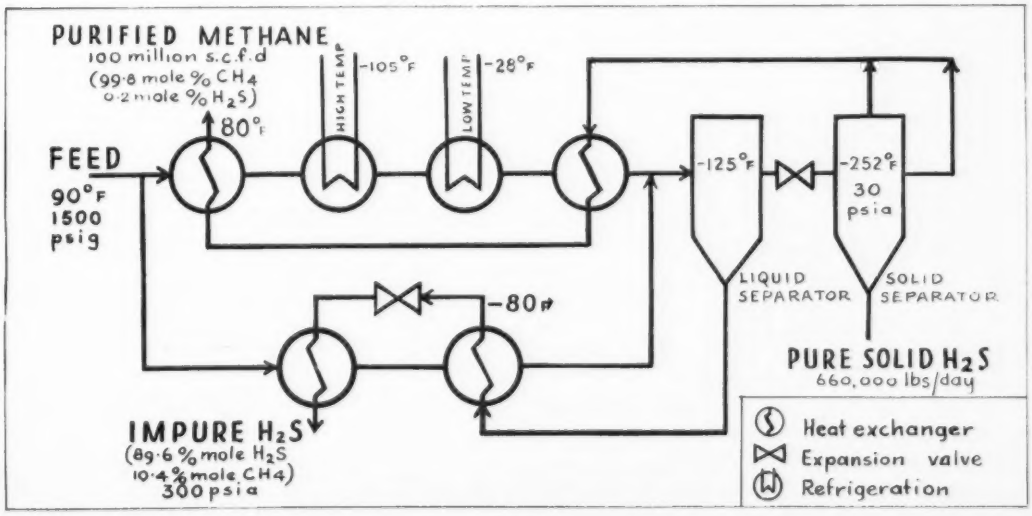


Fig. 7

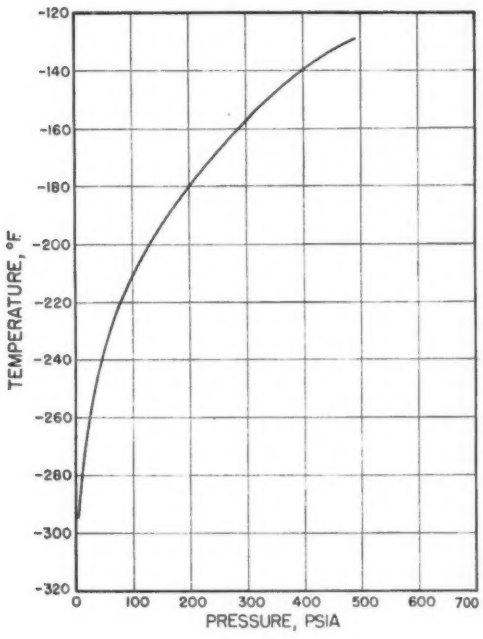


Fig. 8

for the recovery of the methane in the hydrogen sulphide-rich liquid by passing the hydrogen sulphide-rich liquid into a solid separator as with the methane-rich liquid. This is not shown on the flow sheets.

For feed gases having a molecular hydrogen sulphide content below about 7% the flow sheet differs in that there is no liquid separator and the gases are expanded directly into the solid separator. Thus there is no cooling stream of impure hydrogen sulphide and the feed gases are all cooled in the one stream going through a refrigeration unit and the heat exchangers having methane flowing counter-currently.

The conditions of pressure and temperature which must obtain in the solid separator for the three-phase equilibrium to prevail are illustrated in Figure 8. The solid separator must operate at a pressure below 490 p.s.i.a. and a temperature of –130°F, as these are the conditions at which solid hydrogen sulphide first forms. The lowest possible operating temperature is –295°F, when solid methane appears. Within this range the temperature chosen will depend on the purity of methane required. As is shown in Figure 9, the molecular percentage of methane in liquid, vapour, and composite vapour-liquid states increases with a fall in pressure, and hence with a fall in temperature, because the lower the pressure the lower is the corresponding equilibrium temperature.

Another consideration is the temperature in the liquid separator. While the composition of both vapour and liquid in the solid separator is determined solely by the equilibrium conditions of temperature and pressure selected, the composition of the intermediate vapour-liquid mixture is influenced by a third variable—the temperature in the liquid separator. The two middle curves in Figure 9 illustrate the molecular compositions of the vapour-liquid mixtures resulting from two different temperatures in the liquid separator. The left hand curve, indicating lower

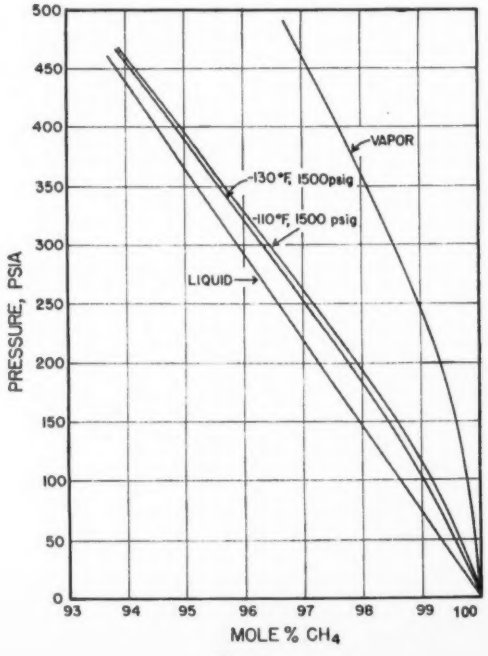


Fig. 9

methane purity, shows the composition of the vapour-liquid mixture resulting from the lower temperature. In the liquid separator the temperature may be varied from –100.1°F to –130.9°F, the advantage of one temperature over another being relatively small and turning mainly on the purity of methane desired. The hydrogen sulphide-rich liquid has a nearly constant molecular composition of 89.4% hydrogen sulphide and 10.6% methane.

Preliminary calculations have been made for methane-hydrogen sulphide mixtures of varying molecular hydrogen sulphide content. These calculations are based on the production of 100 million s.c.f.d. of methane with a molecular methane content of 99.8% and a molecular hydrogen sulphide content of 0.2%.

Heat and material balances for feed gases having a molecular hydrogen sulphide content of more than 7% are given in Table 1. Referring to Figures 8 and 9, the pressure and temperature in the solid separator must be 30 p.s.i.a. and –252°F respectively, for an arbitrarily set temperature of 125°F in the liquid separator, in order to achieve the specified methane purity. Feed gas is assumed to enter the system at 1,500 p.s.i.g. and 90°F. The methane stream from the solid separator is heat exchanged with feed using 10°F approach to the full extent capable by this stream. The hydrogen sulphide stream from the liquid separator is heated to –80°F in the second heat exchanger and expanded to 300 p.s.i.a. before entering the first exchanger. The addition of 5% to the net cooling load required is assumed to account for the heat leakage of the system including heat leakage from the refrigeration units. Pressure drops in the system are not considered.

Since most of the condensation of feed gases takes place at temperatures of about –100°F, two-stage refrigeration is used with methane as a low-temperature refrigerant and ammonia as a high-temperature refrigerant. The evaporation temperature for ethane is –105°F and that for ammonia is –28°F. The condenser temperature for ethane is –20°F and that for ammonia is 100°F. Ethane is directly condensed in the evaporator of the ammonia refrigeration system. It is assumed that the efficiency of the compressors is 75%. The horsepower requirements for refrigeration are minimum values since the cooling capacities of both the methane and the hydrogen sulphide streams are fully exploited for the assumed temperature approach in heat exchangers, excluding the solid hydrogen sulphide.

Table I

H_2S in Feed Mole %	Final temp. of H_2S rich stream	Million Standard Cubic Feet per Day				Refrigeration Load—H.P.		
		Feed gas flow in upper circuit	Feed gas flow in lower circuit	Total feed gas flow	Flow of H_2S—rich gas	Low Temp.	High Temp.	Total
7	80	107.8	0.2	108.0	0.1	486	846	1332
10	80	103.0	8.6	111.6	4.5	382	666	1048
15	80	97.0	22.5	119.5	12.0	139	243	382
20	79	93.0	35.5	128.5	20.6	0	0	0
26	70	90.0	49.5	139.5	32.5	0	0	0
32	63	88.7	65.6	154.3	47.1	0	0	0

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A flow sheet of the process for feed gases having a molecular hydrogen sulphide content of less than 7% is shown in Figure 10 and

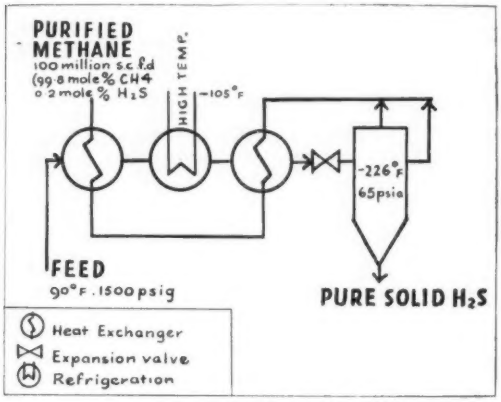


Fig. 10

heat and material balances are given in Table II. With this system the pressure and temperature in the solid separator are –226°F and 65 p.s.i.a. respectively. The ratio of molecules of liquid formed to molecules of vapour is 1 to 100.

The refrigeration loads for the various molecular hydrogen sulphide concentrations given in Tables I and II are plotted in Figure 11.

From this it will be seen that the horsepower requirement for refrigeration rises with a fall in the hydrogen sulphide content of the feed gases till the molecular concentration is as low as 7%. This is because with a lower hydrogen sulphide content the relative amount of hydrogen sulphide-rich liquid from the liquid separator is greatly reduced, the cooling effect of this stream being diminished also. With a feed gas having a molecular hydrogen sulphide content of 7% or less, practically no external refrigeration is required.

The process as a whole could be modified by using solid hydrogen sulphide as a coolant. Alternatively for feed gases having a molecular hydrogen sulphide content of less than 20% but more than 7%, all or part of the hydrogen

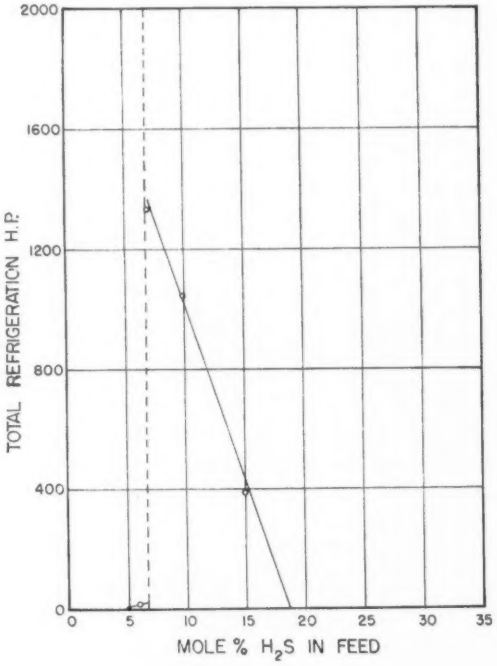


Fig. 11

Table II

H_2S in Feed Mole %	Final temp. of purified methane stream	Total feed gas flow	Output of pure H_2S (lbs./day)	Refrigeration Load—H.P.		
				Low Temp.	High Temp.	Total
2	39	101.9	164,000	0	0	0
4	63	103.8	352,000	0	0	0
6	80	106.0	551,000	0	16.5	16.5

sulphide-rich stream from the heat exchanger might be recompressed and injected into the feed stream to increase its hydrogen sulphide content so that no refrigeration would be required.

Conclusion

There can be little doubt that great interest will be shown in this approach. Nevertheless it is a matter of common experience that many difficulties arise in the practical application of a theoretically sound process. It seems likely that considerable development work would be necessary before a comprehensive cost estimate could be prepared inclusive not only of refrigeration costs, but of other operating costs—among which are of course those of compression—and of capital costs also.

THE HARPENER PROCESS FOR TREATING COKE-OVEN GAS

THE HARPENER PROCESS is one of the many ways of purifying gas by ammonia washing. In the conventional method the quantity of hydrogen sulphide removed corresponds with the equivalent quantity of ammonia in the gas. The Harpener process is designed for treating gas with a hydrogen sulphide content in excess of its ammonia equivalent. Both hydrogen sulphide and ammonia are removed. Furthermore the ammonia content of the washing solution is 7% by weight, which is considerably more than the usual ammonia content of washing solution. Thus steam consumption for the circulation of the washing solution is reduced and the steam requirement per unit of hydrogen sulphide or ammonia removed is in consequence reduced also.

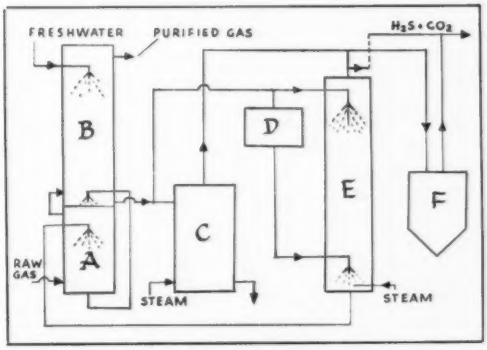


Fig. 12—*Flow Diagram.*

A—Lower Part of Washing Tower. B—Upper Part of Washing Tower. C—First Stripper. D—Used Wash Solution Condenser. E—Second Stripper. F—Saturator.

The flow sheet of the process is given in Figure 12. In the lower part of the washing tower concentrated washing solution from the second stripper is sprayed into the coke-oven gas and increases its ammonia content. With the Harpener process this washing solution usually contains 60-70 grammes of free ammonia per litre, and an equilibrium between the hydrogen sulphide and the ammonia gases is thus achieved. In order to make full use of the concentrated washing solution, when it has been sprayed into the raw gas in the lower part of the washing tower, it is then sprayed into the gases in the upper part of the washing tower, together with fresh water already containing a little ammonia. On leaving the upper part of the washing tower the free ammonia content of the washing solution is 20 grammes per litre, whereas by other processes it is only 10 grammes per litre. Purified gas flows out of the top of the upper part of the washing tower.

When the washing solution finally leaves the washing tower it is initially divided into two streams. One of these goes to the ammonia remover, or first stripper, where ammonia, hydrogen sulphide and carbon dioxide are all driven off, and the other goes to the second stripper, some of it having passed through a

used wash solution condenser. The ammonia-laden effluent from the second stripper is recycled to the washing tower, its ammonia content varying in proportion to the pressure within the first stripper. A higher pressure of course requires a greater consumption of steam.

By recycling a 7% ammonia solution the circulation can be reduced, so as to allow a reduction in the steam consumption per tonne of additional sulphuric acid recovered in excess of the ammonia equivalent contained in the gas. The overall saving in steam consumption is approximately a tonne of steam per tonne of sulphuric acid recovered. Included in this figure for steam consumption is the increased requirement for maintaining the higher pressures in the strippers. Hydrogen sulphide removal under pressure is liable to corrode construction materials: the second stripper, the used wash solution condenser, and the heat exchanger should be made of Hastelloy C, which did not suffer from corrosion in two years of continuous operation, even at temperatures in excess of the given resistance limit of 70°C.

Filtration of Sulphuric Acid Mists

ALONG THE SHIP CHANNEL AT HOUSTON IN TEXAS the high degree of industrialisation has meant that all firms have had to minimise the air pollution for which they are responsible. Only the smallest all-round increase in the amount of pollution contributed would make the atmosphere unhealthy in the extreme. Here the Consolidated Chemical Industries Division of the Stauffer Chemical Company has four brimstone burning contact sulphuric acid plants, and two units for the regeneration of spent alkylation acid, having a total capacity of nearly one-half million tons of 100% acid a year. There are six tail-gas stacks. Together they discharge about 2,200 cubic feet of gas per second. Stack temperatures vary between 150°F and 200°F and gas velocities vary from 15 cu. ft. per sec. to 40 cu. ft. per sec. Such velocities are sufficient to bring about the entrainment of quite large particles of acid mist from the absorption towers. At one time considerable paint damage was caused, especially to cars parked nearby. In consequence the company has been experimenting with a variety of filters, and its findings were summarised by Mr. O. D. Massey in a paper delivered at the Manufacturing Chemists' Association Conference on Air and Water Pollution Abatement in March, 1959.

Sources of Stack Mist

Acid mist in the exit gases may arise from a great number of sources. One of these is poor absorption. As much as ten tons of acid mist may be formed daily at a single acid regeneration plant. It is not definitely known exactly how mist is formed in the absorption towers. Among the factors that play a part are the temperature, strength, and circulation rate of the absorber acid, and whether or not there are dry spots in the packings. Moisture is another cause. In a brimstone burning contact plant this may arise from the presence of hydrocarbons and other organic impurities in the sulphur. Even though the organic substances burn completely, they contribute moisture nuclei to the gas stream beyond the drying tower. This can happen even though the gas as a whole never reaches the dew point. A stack plume may be formed through the chilling on steel duct work of gases containing sulphur dioxide. Mist is often formed by mechanical entrainment, but this is the type most easily removed, as any device which changes the direction of the gas flow will achieve this end. Yet another difficulty is stack spitting caused by the dry and powdery iron sulphate that accumulates in stack ducts. This can get blown over a wide area, and as

it is hygroscopic, it can cause considerable damage. Acid mist of the smallest particle size and the most difficult to remove is that produced when oleum is being made.

METHODS OF DE-MISTING

Cyclone De-Misters

When applied to exit gases these are of limited use, for although they can remove large particles (20 microns), considerable power is needed to remove smaller particles.

Glass Fibre Filters

At the Houston plant several experiments yielded the conclusion that glass fibre filters tend to pack when wet, and although efficiency is high, it is difficult to force the gas through them.

Packed Beds

The adaptation to exit gases of packed beds of coke and quartz rings and saddles has drawbacks with regard to the size of vessels required, the pressure drop, and general efficiency. A 1 ft. bed of 1" berl saddles in a vessel so sized that the gas flow is between 10 and 12 feet per sec. will catch a considerable amount of acid mist with a fall in pressure of only about 1" of water. Higher gas velocities will cause re-entrainment. The quantity of acid mist has not been reduced to the 2 mg/cu. ft. desired without excessive pressure drops and thicker beds. In general a brimstone burning plant not making oleum will have an invisible stack plume when the acid mist content of the stack gases is about 2 mg/cu. ft. or less. Further details are set out below :—

Velocity	*Pres. drop In. of water*	*Mg. H_2SO_4/cu. ft. Inlet*	*Mg. H_2SO_4/cu. ft. Outlet*	*Efficiency %*
7 ft./sec.	3/8	16.5	14.5	12
10 ft./sec.	3/4	18.3	6.4	65
12 ft./sec.	1¼	25.8	11.6	55
20 ft./sec.	3¼	46.7	28.8	38*

* Re-entrainment probably occuring

Vane Filters

Good performance was given by a vane type filter. It consisted of ten staggered rows of parallel vanes having a teardrop shape. They were about ½" wide and ½" apart and were assembled into modules placed in a horizontal run of pipe. Small particles of acid mist in the gas stream are precipitated through the shape and arrangement of the vanes. With a face velocity of 30 ft. per sec. an efficiency of 50% was achieved. When the velocity was increased to 50 ft. per sec. an efficiency of 90% was obtained with a pressure drop of 4" of water. The exit gas contained 2 to 4 mg. of sulphuric acid mist per cubic foot, giving a stack plume which was visible but nevertheless not serious. The results of the experiments are summarised below :—

Velocity	*Pres. drop In. of water*	*Mg. H_2SO_4/cu. ft. Inlet*	*Mg. H_2SO_4 cu. ft. Outlet*	*Efficiency %*
30 ft./sec.	2¼	34.8	16.9	51.4
,, ,,	2	14.2	6.8	51.8
,, ,,	2	28.6	5.2	81.8
,, ,,	2	35.2	3.3	90.6
50 ft./sec.	4	26.3	2.3	91.4
,, ,,	4	18.8	4.1	78.2

The choice of material was unfortunate. The moulded carbon was unsuited to the conditions. At a temperature of 190°F and in the presence of 98% sulphuric acid and possibly traces of nitric acid, the carbon oxidised and finally collapsed. However this by no means indicates that vane type filters are necessarily unsuitable.

Lurgi Type Filters

These patented filters consist of porous ceramic thimbles through which the gases pass. The performance of the filter was excellent, and in acid regeneration plants the acid content of the outlet gas was consistently reduced to 1 mg. per cu. ft. The drop in pressure was 7" to 11" of water. Test results were as follows:—

Velocity	*Pres. drop In. of water*	*Mg. H_2SO_4cu. ft. Inlet*	*Mg. H_2SO_4 cu. ft. Outlet*	*Efficiency %*
5 ft./sec.	9	15.8	1.5	90.5
,, ,,	10	59.6	2.8	95.3
,, ,,	10	54.9	0.8	98.6
,, ,,	8	21.4	6.0	72.0
,, ,,	8	17.5	4.5	75.0

Lurgi filters are, however, expensive to maintain. The ceramic tubes may be broken. The required area is large and so is the

pressure drop. Tubes can now be obtained from American manufacturers and are an alternative to those made in Germany.

Knitted Wire Mesh Filters

These are unique in their large surface area and in their free volume and light weight. As used by the company the lower stage has high density mesh of 12 or 14 lbs. per cu. ft., and the upper stage has a density of 5 or 7 lbs. per cu. ft. Both pads vary from 4" to 8" in thickness, and the stages are generally separated by a distance equal to three-quarters of the vessel's diameter. An illustration is given in Figure 13.

Within the range of the correct gas stream velocity, a layer of entrained liquid is held up between the wires of the filter. This liquid scrubs the gas stream and by increasing its

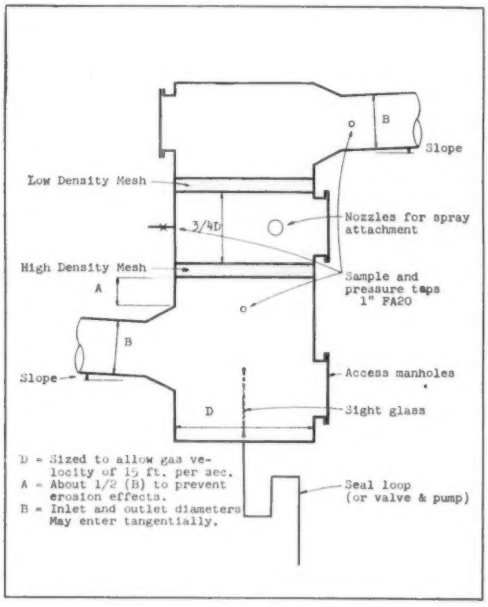


Fig. 13

velocity makes the impact of the acid mist particles greater. As the volume of liquid grows larger, its weight out-balances the pressure of the gas stream, and it drips out. If the velocity is too high the scrubbing liquid will be re-entrained. The optimum velocity depends both on the nature of the gas stream and of the entrained liquid.

One three-stage filter was tried with a thick pad of smaller diameter wetted by spray nozzles, as it was hoped that the resulting high velocity of scrubbing action would asborb the fumes from an oleum tower. The experiment was a failure and the particle density of the stack plume showed scarcely any change.

The experiments with two-stage wire mesh filters indicate that the proper velocity of the gas stream in the duct approaching the filter is 15 to 18 ft. per sec. although it may fall to as low as 10 or 11 ft. per sec. without an unacceptable fall in efficiency. If too low an efficiency is achieved at these velocities, thicker or more dense wire pads may be used. This will naturally increase gas pressure behind the filter; and with a rate of gas flow of 1,000 cu. ft. per minute each additional inch of water pressure will require an extra 0.158 h.p.

The table below sets out the results of tests. When making 98% acid, the stack plume is rendered practically invisible, and the acid mist content of the exit gas is reduced to 1 or 2 mg/cu. ft. with a pressure drop of only 1.5" to 2" of water, though the precise efficiency achieved will turn on the acid mist content of the filter intake. Although the filters have not succeeded in removing the smaller particles from oleum mist, this task is beyond ordinary entrainment separators.

Velocity	*Pres. drop In. of water*	*Mg. H_2SO_4 cu. ft. Inlet*	*Mg. H_2SO_4 cu. ft. Outlet*	*Efficiency %*
12 to 15 ft./sec.	1	8.8	0.70	92.5
,,	¾	4.1	0.74	82.0
,,	1¼	13.8	0.92	93.4
,,	1¼	66.9	0.77	98.9
,,	1½	32.5	0.98	97.0
,,	1½	13.0	0.76	94.1

The company's experience of corrosion is limited in that the oldest wire mesh filter in use at Houston is less than two years old. This filter's lower stage was made of Carpenter 20 alloy and showed considerable corrosion after

14 months, yet it appears that most of the damage may have been caused by weak sulphuric acid during some plant-scale experiments. The next filter installed was made with Hastelloy wire mesh. The difficulty with this alloy is that although it is immune to 98% sulphuric acid it will not resist traces of nitric acid. Brimstone burning sulphuric acid plants give off traces of nitric acid of the order of only a few parts per million, but regeneration plants have considerably more nitric acid in the stack drip. In any event, three months of operation destroyed the lower Hastelloy B pad. The upper part, made of Carpenter 20 alloy, was not noticeably harmed. The Hastelloy C wire mesh filter in a brimstone burning contact plant appeared to be in perfect condition after one year's service and is still performing satisfactorily. The relatively inexpensive alloy 20 appears to be the most practical material to use, assuming that the corrosion experienced in one instance may have been due to other factors. Carpenter 20 grids were used in all cases above and below each filter pad. No appreciable corrosion has occurred on the grids which were of rods $\frac{1}{4}$" in diameter.

Knitted wire mesh filters are made by several manufacturers. The following table gives some typical specifications :—*

Density Lb. cu. ft.	*Surface area Sq. ft. cu. ft.*	*Free volume Approx. %*	*Thickness† Ins.*
14	120	96	4
12	115	97	4
9	85	98	4, 6
7	65	99	6
5	45	99	6

* Wire sizes available from 0.003 to 0.016 ins. Usually 0.011 in. used as in above data

† Thickness varies with efficiency desired and allowable pressure drop

Conclusions

As compared with wire mesh filters, chemical absorption units and electrostatic precipitators involve large plant and a high capital cost with a low rate of return. Claims for damage from sulphuric acid mist have practically ceased since the introduction of wire mesh filters. It is these that the company favours.

The Use of Glass for Acid Cooling

SOME SIX YEARS AGO Scottish Agricultural Industries Ltd. had to build a cooler for a Petersen sulphuric acid plant. For de-nitrated acid, lead is the normal material to use, and for nitrous acid cast-iron is generally adopted, the preference being for vertical cast-iron pipes. However at the time the price of lead was high and vertical cast-iron pipes were not available in the United Kingdom. Furthermore experience had shown that neither of these materials was entirely satisfactory. The use of boro-silicate glass was therefore considered. It was expected that this material would be immune from chemical attack from both the de-nitrated and nitrous acids, free from external corrosion, and unaffected by scale formation from the cooling water. While the heat transfer coefficient is considerably less for glass than for new cast-iron, glass does not suffer from a decline in the rate of heat transfer which in the instance of cast-iron coolers arises from the formation of external rust scale.

It was necessary to cool 45 grammes per minute of de-nitrated sulphuric acid of 76-80% concentration from 120-140°C to 35°C, and 375 grammes per minute of sulphuric acid of the same concentration, but containing 1.5-3.5% nitric acid, from 90-100°C to 35-40°C. The arrangement provided for a gravity flow from elevated towers resulting in a maximum pressure at the base of the coolers of 17 p.s.i. The glass coolers originally installed took the form of a number of banks of serpentine pipework involving 2.7 miles of piping of 3" bore and 3 mm. wall thickness. Each bank was four pipes wide and 17 pipes high. Cooling was by fresh water circulating over the pipes and through an atmospheric tower. An illustration of the type of joint

initially installed in the cooler is given in Figure 14.

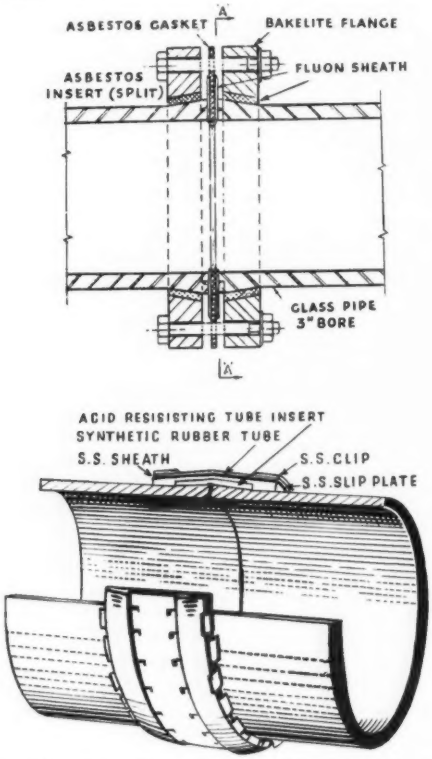


Fig. 14—Top. The type of joint originally used in the coolers. Bottom. The new joint.

Operating Experience

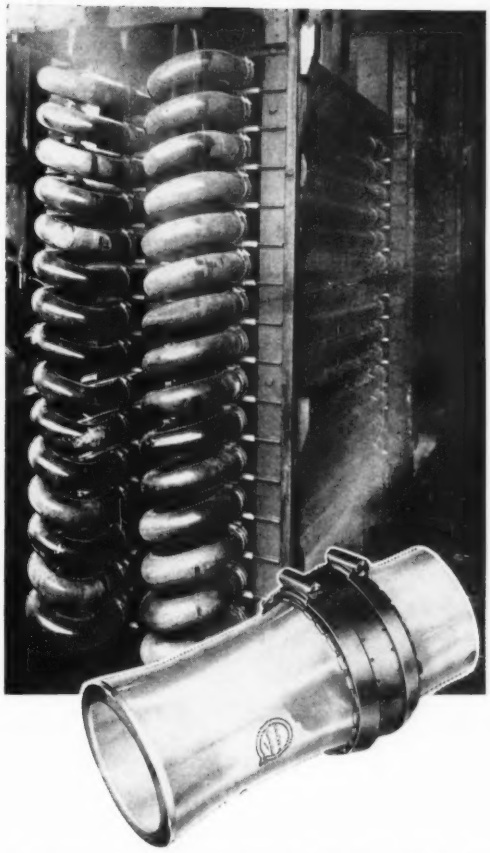
In the first few months of plant operation serious breakage of the glass pipes was experienced. This was a direct result of the form of glass construction used in which a 180° bend and two lengths of pipe of approximately 11′ in length were formed in one piece to make an elongated "U". As a result a slight inaccuracy in installation caused severe stress in the bends. The broken sections of glass were replaced with standard straight lengths of tube and joined by short "U" bends at the end. Since then breakage of glass pipes has been almost unknown. The glass pipes have not suffered at all, either from internal attack from the acid or from external scale, the only change being a slight discolouration.

However, leaks from the pipe joints continued. The asbestos joining material within the Fluon sheath was very hard and did not readily conform to variations in the face between the glass pipes. The Bakelite flanges became fractured owing to water absorption by the Bakelite itself and also by the asbestos of the inserts under the flanges.

To solve these problems various modifications were tried. Amongst these were the use of a special form of Bakelite having a low water absorption, cast iron flanges, and softer gasket material such as butyl rubber or plasticised PVC enclosed in a Fluon sheath. All the modifications suffered from the basic disability that the tightness of the joint was dependent on drawing together the end faces of the glass tubes. Where the two faces were not exactly parallel, either on account of lack of uniformity of the glass itself or incorrect alignment of the pipes, the pressure on the gasket was not the same across its whole face. Any movement of the pipes through expansion or contraction soon resulted in leaks. Furthermore even the special Bakelite suffered from some water absorption. There was also doubt as to whether the angle of the tapered section at the end of the tubes was sufficiently steep, the standard having been changed after the time at which these units were made.

New Tube Joints

Owing to the failure of other expedients, a new joint was designed. An illustration is given in Figure 14. It takes the form of a pliable sleeve enclosed in a metal fixing band with a number of fingers, which is tightened by means of a clip at each end. Experiments showed that the most appropriate acid resistant and pliable material for the conditions was much too expensive to use for the complete sleeve. Acid resistant material is used only for the seal across adjoining pipe sections, and the remainder of the pliable sleeve is made in any resilient material suited to the temperature conditions, such as Hypalon or butyl rubber. Although the fixing joint and clips were made in stainless steel to guard against corrosion



End view of a bank of acid coolers fitted with the new joint.

from the cooling water, in different conditions these might be made of other materials.

No tensile stress is transmitted to the pipe as a result of tightening the coupling. As the joint remains flexible, movement from thermal or other causes neither brings about tensile stress nor does it affect the tightness of the joint. In fact, any lateral movement due to end thrust on the bends will tend to tighten the joint. As the tube joint is very much smaller in diameter than the flange type, coolers can be constructed with pipes at much closer pitch, and for a given surface area a more compact cooler is obtained requiring less head for acid flow and offering improved conditions for water distribution.

A Patent Application has been filed and the joint is now to be used in a range of sulphuric acid cooling equipment made and marketed by Q.V.F. Limited of Stoke-on-Trent. Although designed for glass pipes, the joint would be suitable for pipes of any material of low tensile strength, such as stone-wear, carbon, silicon, or iron.

Cooling Tests

The introduction of the new joint enabled the coolers to be reconstructed at an overall height of 7′, the banks consisting of 15 tubes, as opposed to an overall height of 13′, the banks consisting of 17 tubes. In addition to the obvious advantage of greater accessibility, the more compact arrangement is of considerable benefit in terms of water distribution. With the old arrangement the 5½″ gap between pipes, though assisted by narrow strips of timber beneath each pipe, resulted in excessive splashing and in consequence poor contact at the lower levels. With the new arrangement the gap between pipes is only 1½″ and a uniform film of water covers all tubes in the cooler.

The following table sets out typical test results obtained on one bank of the cooler :—

Acid :	Acid flow	55 grammes/minute
	Acid velocity	1.3 feet/second
	Specific gravity	1.67
	Inlet acid temp.	71°C.
	Outlet acid temp.	42°C.
	Acid temp. difference	29°C.
Water :	Water flow	150 grammes/minute
	Inlet water temp.	27°C.
	Outlet water temp.	34°C.
	Water temp. difference	7°C.
Heat transfer :	Overall heat transfer coefficient	27 CHU*/sq.ft./hr/°C.

*Approx. 1.8 BTU

The heat transfer coefficient obtained during the test of 27 CHU/sq.ft./hr/°C compares favourably with a figure of 27/28 CHU/sq.ft/hr/°C commonly quoted for 3″ bore cast-iron cooler pipes at a similar velocity, this latter figure being a practical one taking into account scale build-up on the outside of the pipes.

This article is based on a paper presented by J. P. A. McDonald and G. B. Whyte of Scottish Agricultural Industries Ltd. to the International Superphosphate Manufacturers Association's Technical Committee.

Automatic Phosphorus Pentasulphide Manufacture

Phosphorus pentasulphide (empirically P_2S_5), is a highly corrosive chemical formed by the interaction of molten phosphorus and molten sulphur. Its most important uses are for oil additives, insecticides and ore-flotation agents.

The chemical has been made for many years at the Oldbury works of Albright & Wilson (Mfg) Ltd., who are the only producers of phosphorus pentasulphide in the United Kingdom. Until late last year the materials had to be manhandled at most of the production stages. Recently, however, the old plant has been replaced by an automatic one providing for continuous production, higher capacity, a better final product and greater safety from the serious hazards of fire and explosion, while also halving the size of the labour force and ensuring much cleaner working conditions. The movement of chemicals between the various units of the plant is directed from a central control panel and is shown graphically on it by a visual flow diagram. The only hand operations now involved are unloading the raw materials, filling the drums with phosphorus pentasulphide, and despatching the drums to other parts of the works.

Molten sulphur, which must contain no bituminous compounds, iron compounds, or moisture, is initially stored in two 65-ton cast-iron vessels where it is maintained in a molten state by steam. Phosphorus is received as a solid. It is melted in its tanker and moved into a 6-ton storage vessel by hot water displacement. The sulphur and phosphorus are pumped from storage through heated pipes into separate weigh-measure vessels and thence into one of two 2,000-gallon cast-iron reactors heated to 450°C. The reaction is exothermic and there is a danger that the phosphorus may vapourise and escape through the water-sealed vent pipes. There is no heat recovery and the temperature is determined by the rate of flow of the sulphur and phosphorus. The flow rate of both chemicals is electronically controlled. When the correct amounts of sulphur and phosphorus have entered the reactor an alarm bell tells the operator to stop the feed pumps.

The product is then driven into an electrically-heated cast-iron holding vessel, where it is sampled and analysed. If necessary, adjustments are made to the flow of chemicals into the reactor in a subsequent batch to provide the required phosphorus content of 27.6% in the phosphorus pentasulphide. Carbon dioxide gas, which drives the pentasulphide

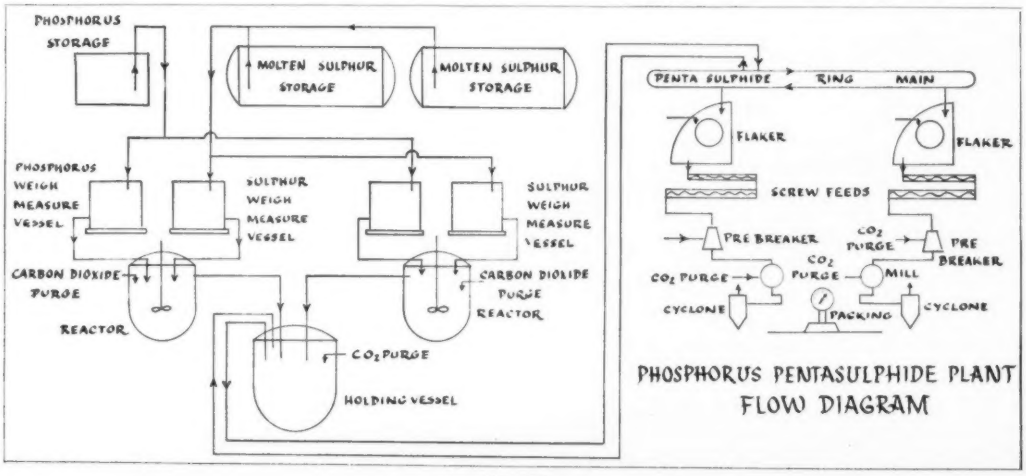
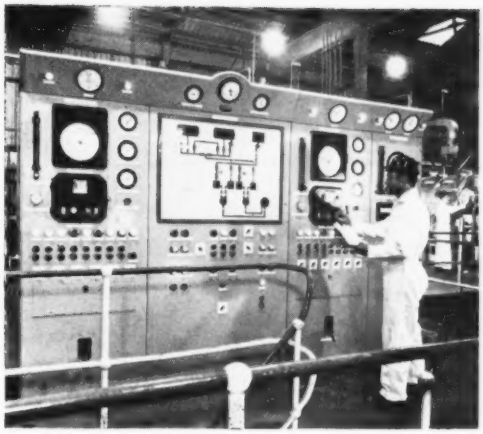


Fig. 15



The control panel of the new Phosphorus Pentasulphide plant at Oldbury of Albright & Wilson (Mfg) Ltd.

from the reactor to the holding vessel, continually purges the entire system to lessen the fire hazard.

From the holding vessel the pentasulphide passes into a mild-steel ring main electrically heated by blankets round which it is continuously circulated and from which it is drawn off on one of two flaking machines. As it leaves the ring main, the liquid flows over a water-cooled roller, breaks off the roller in flakes or slivers, and drops onto a water-cooled screw conveyor. This lowers the temperature of the pentasulphide and takes it to a pre-breaker, where the flakes are reduced in size and passed to a mill. This section of the plant is equipped with automatic explosion detecting devices.

The phosphorus pentasulphide powder is then loaded into drums and taken away for use in the production of thiophosphates. The manufacture of oil additives and organophosphorus insecticides from thiophosphates is also carried out at the Oldbury works.

Sulphur Dioxide as an Oxidising Agent

THE ROLE OF SULPHUR DIOXIDE in vapour phase oxidations of alkylated benzenes with vanadium oxide as a catalyst was the subject of a paper delivered at the 136th National Meeting of the American Chemical Society by Thomas H. Strickland and Dr. Alan Bell, both of Tennessee Eastmann. Past research seemed to indicate that sulphur dioxide inactivates vanadium oxide catalyst and that small amounts could at most be used as a moderator for the "hot spots" which appear on the catalyst when air is the source of oxygen. However it has now been found that sulphur dioxide can also work as a major reactant, being the oxidising agent. Compounds oxidised with sulphur dioxide over vanadium oxide (on alumina) include toluene, *m*- and *p*-xylenes, *tert*-butylbenzene, ethylbenzene, butylbenzene and methylcyclohexane.

Both the yield and the product depend upon the temperature. For example, toluene is oxidised to benzaldehyde with a 90% yield at 315°C, and to benzoic acid with a 95% yield at 410°C. Other monoalkylated benzenes are also oxidised to benzoic acid. Dialkylated benzenes give their corresponding toluic or phthalic acids. Mr. Strickland claimed that in some respects sulphur dioxide is better than air for these oxidations. For instance, oxidation of toluene by air gives benzaldehyde and benzoic and maleic acids, maleic acid resulting from the degradation of the benzene nucleus, whereas oxidation by sulphur dioxide gives either benzaldehyde or benzoic acid, but no maleic acid.

In vapour phase catalytic reactions hot spots may occur in the catalyst bed owing to excessively rapid oxidations and in consequence catalyst inhibitors are usually added in small quantities either before or during the oxidation. These inhibitors are generally sulphur oxides or organic sulphur compounds. Sulphur dioxide is an efficient inhibitor,

especially when used with a vanadium oxide catalyst, as determined by the California Research Corporation (U.S. Patent 2,574,511). Usually 0.01 to 15% by weight of sulphur dioxide works satisfactorily, although its use is restricted to oxidations having a stoichiometric excess of oxygen. Thus sulphur is not a reagent in these reactions. Some have reported that sulphur dioxide alone deactivates vanadium oxide catalyst.

With this earlier knowledge behind them the chemists' reaction conditions for sulphur dioxide oxidations were arbitrarily selected. The first experiment was with a 4:1 molecular ratio of toluene to sulphur dioxide and the reactants were passed over vanadium oxide catalyst at 350°C with a contact time of five seconds. The products under these conditions are hydrogen sulphide, water, elemental sulphur and a trace of benzoic acid. But at a temperature of 380°C an 80% yield of benzoic acid is achieved and no catalyst hot spots occur.

The contact time, the molecular ratio of hydrocarbon to sulphur dioxide, and diluent additions all have some effect on the reaction, but the most important consideration is the temperature. Between 390°C and 430°C the only product is benzoic acid. The maximum temperature preferred is 410°C, at which both the yield and the conversion of hydrocarbon are 95% when based on sulphur dioxide and 75% and 28% respectively when based on toluene. The relatively low conversion rate does not take into account the large excess of toluene used as a diluent. A contact time of between three and five seconds suffices for the full temperature range. Yields of benzoic acid from monoalkylated benzenes using sulphur dioxide at a temperature of 410°C are given below :—

TABLE I

	Based on Hydrocarbon		Based on SO_2	
	Yield%	*Conversion%*	*Yield%*	*Conversion%*
Toluene	75.0	28.0	52	45.0
Ethylbenzene	31.3	17.1	41	41.0
Isopropylbenzene	30.8	9.0	37	37.0
Butylbenzene	21.0	7.3	12	10.5
tert-Butylbenzene	5.5	0.7	95	95.0

The effects of diluents vary. With toluene practically no yield changes occur when the reaction mixture is diluted with nitrogen by as much as 2%. If excess toluene is used and considered an inert diluent, it is recovered unchanged. But with dialkylated benzenes diluents are more important. Both excess hydrocarbon and nitrogen reduce yields. For example, an excess of four molecules of *p*-xylene per molecule of sulphur dioxide reduces yields of terephthalic acid almost to zero as opposed to 2.2% under optimum conditions in addition to *p*-toluic acid and *p*-tolualdehyde. Mere traces of nitrogen cause carbon deposits on the catalyst bed and slow down the gas flow through the reactor.

The St. Gobain Sulphur Burner

AT THE SEPTEMBER MEETING of the International Superphosphate Manufacturers' Association in Stockholm, Monsieur J. M. Lerolle described the sulphur burner developed by St. Gobain because of the lack some ten years ago of a reliable burner to produce a gas having a sulphur dioxide content in excess of 17%, the quantity of sulphur dioxide per hour being only about 500 kg. With so small a flow of sulphur, the disadvantage of mechanical atomisation, which is achieved by pumping liquid sulphur through an orifice small in diameter, is that so narrow an orifice is required that any minute particle will suffice to block it. With atomisation by air the orifice need not be so small, since both sulphur and air pass through it. St. Gobain burners can produce a gas having an 18% sulphur dioxide content with complete combustion of the sulphur. Their flexibility is great. The output of a burner designed to produce 250 kg. of sulphur dioxide per hour may be varied between 100 and 400 kg. per hour. A burner with a capacity in excess of 6 tonnes of sulphur

dioxide per hour is under construction, and the company has already built burners having capacities of 2 and 4 tonnes of sulphur dioxide per hour. Two burners having a capacity of 250 kg. per hour have worked successfully in St. Gobain's own factories. A customer has been satisfied with the operation of a small burner with a capacity of even less than 100 kg. per hour. Another burner has been built to use either sulphur, or hydrogen sulphide, or both simultaneously, and has operated well. St. Gobain burners may be used for making sulphuric acid, liquid sulphur dioxide, or sulphur dioxide derivatives.

The Burner

Molten sulphur is pumped slowly through a central pipe around which there is a jacket containing air pre-heated to the optimum temperature, which is between the melting point of sulphur and that at which its viscosity increases sharply—about 130°C—and compressed to about 300 gr. per sq. cm. Orifices direct the compressed air in a series of streams tangentially onto the melting sulphur. The resulting air and sulphur emulsion is squirted into the combustion chamber, where the expansion of the air contained in the emulsion atomises the sulphur. Combustion air, generally pre-heated, is here introduced, and all of the sulphur is burned. About 96 or 97% of the total air used is introduced at the combustion chamber stage, the remaining 3 or 4% being atomisation air.

The principal difficulty is one of temperature control. It is necessary to maintain the molten sulphur at the temperature of its minimum viscosity—about 150°C—up to the point at which it enters the burner. Within a few degrees its viscosity increases in the proportion of 1 to some 10,000. If the temperature of the burner nozzle is not closely controlled, the sulphur may either block the orifice or shoot out as filaments. The problem is complicated by the fact that the nozzle is subjected to the considerable heat from the flame. It may be fitted with a steam jacket, but this must not be too large, as the greater the jacket's external surface the more heat is absorbed by it. The nozzle may be cooled by the inflow of combustion air ; and screens may also be placed to check radiant heat. All three methods are in fact used. The temperature of the sulphur in the burner itself may be easily regulated by means of a steam jacket around the furnace and by adjusting the temperature of the atomisation air.

For the larger burners, many experiments with fluid flow, steam jackets, and protection screens were necessary before the thermal problems were solved. With burners consuming more than 1 tonne of sulphur per hour, the emulsion of sulphur and compressed air is achieved by blowing the atomising air both onto the inside and the outside of a hollow cylinder of molten sulphur instead of merely onto the outside of a solid one.

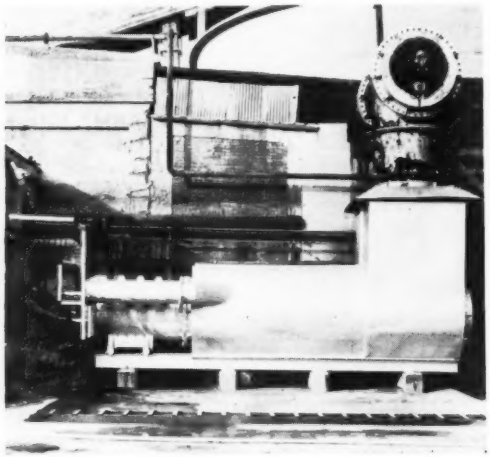
The furnace itself is cylindrical with a steel casing and a refractory brick lining. To permit the free expansion of materials, it must be especially constructed : when sulphur dioxide of 17 or 18% concentration is being made the internal temperature is about 1,400°C. Near the exit the furnace is fitted with a series of baffles to ensure the homogeneity of gas temperature and composition. After the combustion chamber there is usually a waste heat boiler when the capacity of the plant is sufficient to warrant it.

Other Components

The sulphur melter may be either with or without stirring equipment. If there is no filtration, molten sulphur storage may bring about some purification. The molten sulphur pump is of the gear type and is driven by an electric motor fitted with a governor. Its flow rate remains very steady, even in the event of a pressure increase brought about by a change in the viscosity of the molten sulphur. The pump rotates slowly and is in consequence very strong. Compression of the atomisation air is by a Roots type compressor. The atomisation air is heated either by steam or by any hot fluid. Compression of the combustion air is mainly controlled to suit the pressure drop in the circuit after the burner.

The Chemipulp-KC Sulphur Burner

A new sulphur burner was developed and tested by the Kimberly-Clark Corporation of Neenah, Wisconsin, in 1954. Its design and sale for commercial application are handled by Chemipulp Process Inc. of



General view of a Chemipulp sulphur burner installed at the Port Alice works of Alaska Pine & Cellulose Co.

Waterton, New York, and Chemipulp Process Ltd. of Kingston, Ontario. The burner is compact and is made in a wide range of sizes with daily capacities from 2.5 tons to 50 tons of sulphur. Daily production can be altered between 50% and 110% of the plant's rated capacity by a simple adjustment of the sulphur pump's stroke and of the air supply, and the burner makes sulphur dioxide in concentrations of between 12 and 18.5%. Another feature is that both bright and dark sulphur may be used, as the burner, which operates between 2,100°F and 2,400°F, oxidises the bituminous material in the dark sulphur and the remaining deposit can be blown out periodically.

Molten sulphur is pumped from the storage pit through steam-jacketed pipes through the steam-jacketed nozzle into the burner itself, which is cylindrical in shape and has a refractory lining. Compressed air is piped to the spray nozzle assembly and is used to atomise the sulphur. Combustion air is preheated in being drawn through a jacket surrounding the burner, generally by an induced draft fan, although a compressor has been successfully used. From the jacket the combustion air passes into the cylinder through a series of ports and the sulphur is burned in suspension. The relatively small mass of the burner means that the average combustion temperature is reached quickly and the formation of sulphur trioxide is thus minimised. Stopping the burner is instantaneous : there is no residual pool of sulphur to be burned ; and gas of full strength is made without sulphur sublimation up to the moment of shut-down. There is a gas analyser and recorder which controls the burner.

The Chemipulp burner is already widely used in the pulp and paper industry in both the U.S.A. and Canada, where varying concentrations of sulphur dioxide are required,

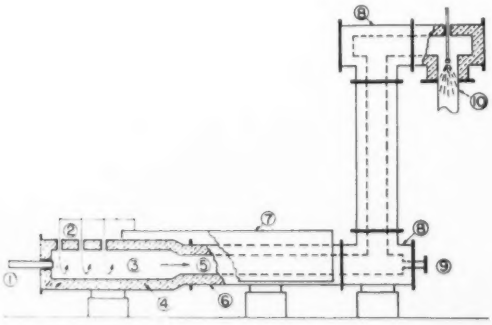


Fig. 16

1. Sulphur feed nozzle. 2. Hot air ports. 3. Tube enlargement for small burners. 4. Refractory lining. 5. Main tube. 6. Steel shell. 7. Jacket or hood for hot air. 8. Tees or elbows. 9. Sight glass—each end. 10. Primary spray cooler or hot gas line.

and is now being adopted in other industries and other countries. In Great Britain a patent covering the burner has recently been granted to the Kimberly-Clark Corporation.

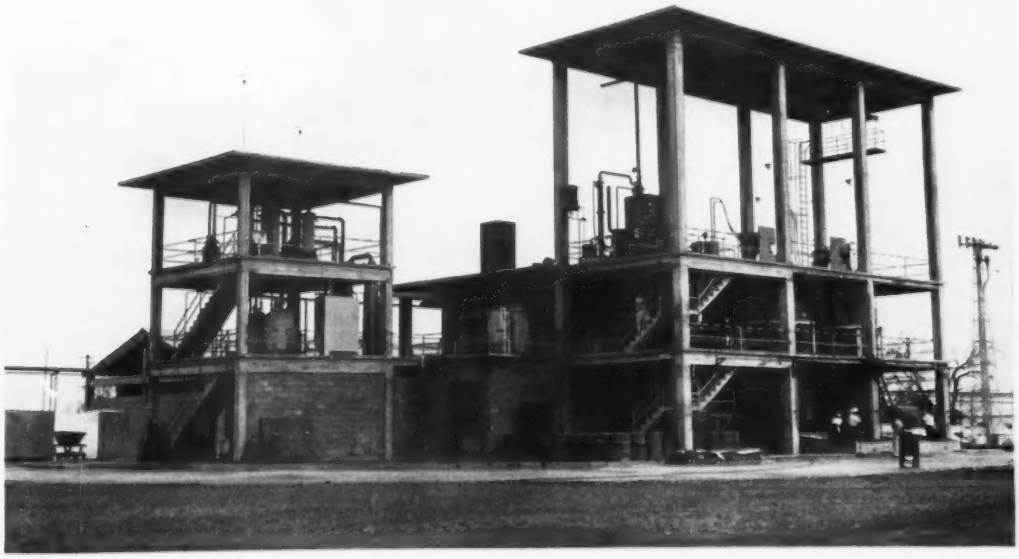
CARBON DISULPHIDE MANUFACTURE BY THE ELECTRIC PROCESS

MOST OF THE WORLD'S CARBON DISULPHIDE is still made in retorts, as the earlier electric furnaces could be used only in those countries in which the cost of electricity was very low. Ing. A. Maurer, S.A. of Berne in Switzerland, who specialise in the design and construction of complete viscose and acetate plants for staple fibre, filament and film, and polyamide and acrylic fibre plants, are one of the many builders of electric process carbon disulphide plants. The company claims that with its plants the prime costs of making carbon disulphide could be 15-25% less than with retorts, the precise figure depending on local conditions. Ing. A. Maurer has been building plants since 1951 with capacities varying between 2.5 tonnes and 28 tonnes of carbon disulphide daily.

Standard Plant

If the carbon contains as much as about 5% of moisture, and in addition, too much volatile matter, it is necessary to dry it initially in a simple roaster. The carbon is brought to the furnace by a skip and is fed through a hopper by which the furnace may be charged without interruption of the process: the hopper is separated from the furnace by a gas-tight valve. Molten sulphur is pumped from a melting pit through steam-jacketed pipes to the sulphur feeder, which serves to control the furnace's sulphur intake. From here it flows through several inlets to the lower part of the furnace.

The temperature of the furnace is the same as that prevailing in a retort—800 to



General view of a carbon disulphide plant installed by Ing. A. Maurer, S.A. The plant has a daily capacity of 10 tons and was commissioned in 1958 for Quimica Industrial de Monterrey S.A., Mexico.

1,000°C; and the furnace is, of course, completely sealed also. It consists of a shell of welded iron lined with insulating and fire bricks of the normal size. The single-phase electric current is transmitted by simple electrodes to the carbon filling, which is heated by the resistance it offers to the passage of the electric current. The voltage varies between 40 and 150 volts and is regulated by a variable voltage transformer: the furnace is easily controlled by voltage adjustment. One man may operate a plant with a capacity of 20 tonnes per day. There are no disadvantages in shutting down the furnace, which can be re-started in 24 hours.

The sulphur vapour contained in the effluent gas is precipitated in the sulphur scrubber and returned in molten form to the melting pit. The remaining gas, consisting mostly of carbon disulphide, passes through water-cooled condensers, and the resulting raw liquid flows into storage tanks. Should the normal cooling water be too warm, the carbon disulphide gas may be passed through a refrigerator. Oil absorption is used to separate hydrogen sulphide and other incondensable gases, and the remaining carbon disulphide is thus recovered. From the raw carbon disulphide storage tanks the liquid flows continuously into the distilling plant. The distilled product is of the quality required for rayon manufacture.

Consumption and Costs

The following figures obtain when the carbon used is in the form of charcoal, when the carbon disulphide is recovered from the incondensable gases in the oil absorption plant, and when the sulphur in the crude carbon disulphide gas flow is recovered by distillation.

Sulphur (99%)	...	900-950 kg. per 1,000 kg. CS_2
Charcoal (roasted)	...	220-250 kg. „ „ „ „
Power consumption at the entrance of the furnace	...	1,000-1,250 kwh. „ „ „ „

The furnace requires cleaning every one to three months, depending on the quality of the raw materials consumed, and the furnace lining need be overhauled only once a year, the repair costs being practically negligible. The shell of the furnance lasts for an unlimited period, nor do the other furnace components need to be renewed, whereas retorts of the best construction generally last for only 10 to 16 months and their replacement is always costly. Finally, building costs are low, since the plant can be placed in the open.

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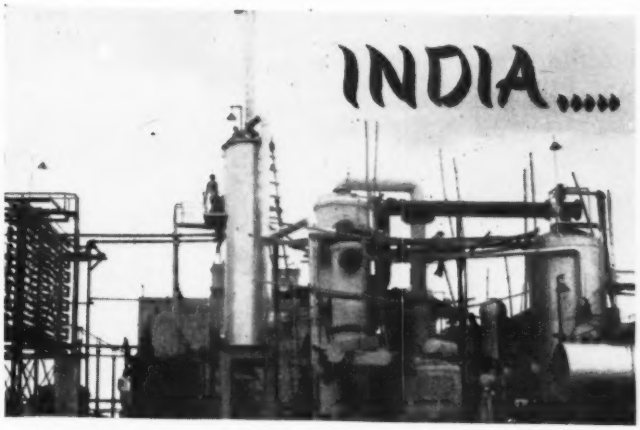

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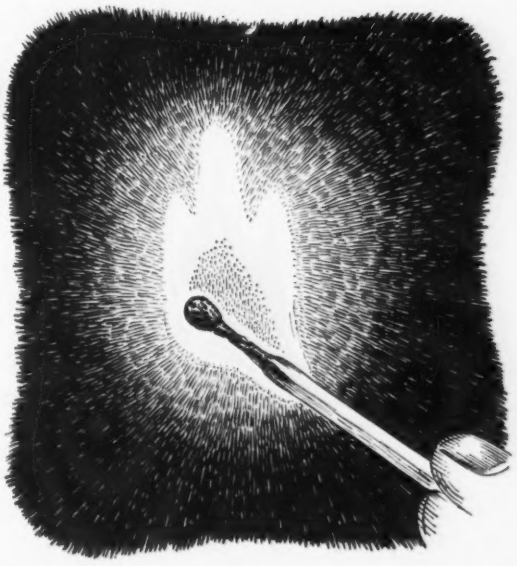

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